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Published in:
Geophysical research letters

DOI:
10.1029/94gl00177

GEOPHYSICAL RESEARCH LETTERS, VOL. 21, NO. 6, PAGES 445-448, MARCH 15, 1994

Bond $^{13}C/^{12}C$ ratios reflect (palaeo-)climatic variations

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Abstract. Stable isotope ratios of hydrogen, oxygen, nitrogen and carbon can serve as (palaeo-) environmental indicators [eg, Ramesh et al., 1986]. ^2H and ^{18}O have the clearest relationship with precipitation and temperature, while the sensitivity of carbon is thought to be far less pronounced, and understanding is not complete. Carbon isotopic variation in ecosystems is mainly due to photosynthesis in plants, and passed on in the foodweb without much overall modification (this enables palaeodiet reconstructions using archaeological bone [Schwarcz, 1991]). Using radiocarbon databases [Van der Plicht, 1992] which also contain ^{13}C data, we have compared a number of European countries for geographical variation in $^{13}C/^{12}C$ ratio of archaeological wood, charcoal and bone samples. We find similar trends for all three materials. A significant trend from northwestern to southern Europe exists in the plant samples, which we relate to climatic differences influencing $^{13}C/^{12}C$ ratios during carbon fixation. This shift passes through the food web, and is thus found in the bone samples, which makes it possible to use accumulated bone stable isotopic data for palaeoclimatic reconstructions.

Introduction

Plants turn atmospheric CO_2 (present-day $\delta^{13}C \sim -8‰$; where $\delta^{13}C = [(^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{PDB}) / (^{13}C/^{12}C_{PDB})] \times 1{,}000$ per mil) into organic matter during photosynthesis, thus drastically modifying the $^{13}C/^{12}C$ ratio. C_3 plants such as trees have an average final $\delta^{13}C$ of about $-27‰$ (range -20 to $-37‰$). Many attempts have been made to explain observed variations in terms of environmental factors [eg, Ramesh et al., 1986; Tieszen, 1991; Epstein and Krishnamurthy, 1990; Wilson and Grinsted, 1977], but with only limited success so far for two reasons. i) The underlying molecular mechanism of isotopic fractionation during photosynthesis is only understood to a limited degree [O'Leary, 1980]. ii) Evidence for systematic variation comes from studies, each of which samples quite specific environmental circumstances, resulting in different data sets not necessarily easily related to each other. For example, isotopic differences exist within the growth of single tree rings [Leavitt and Long, 1991], and between coniferous and deciduous trees [Stuiver and Braziunas, 1987]; Late-Glacial wood from south Central Europe shows a $\sim 1.5‰$ increase concomitant with climatic improvement at the beginning of the Holocene [Becker et al., 1991], but the evidence for a tree $\delta^{13}C$-temperature link is contradictory [Long, 1982; Stuiver and Burk, 1985]. Even under laboratory (growth chamber) conditions the results are conflicting [Ramesh et al., 1986]. High-elevation trees that are highly stressed due to marginal growth conditions, such as Bristlecone Pine, show abnormal $\delta^{13}C$'s [Stuiver and Braziunas, 1987; Linick et al., 1986]; and in a study by Yapp and Epstein [1977] climatic influences seem unclear in 9,500-22,000 BP wood. A strong dependency on latitude was found by Stuiver and Braziunas [1987] in a North American 2000-yr-long record of wood cellulose: increasing latitude results in more negative $\delta^{13}C$'s, with probably relative humidity and temperature as the controlling factors. It seems that the interactions between the many environmental variables result in a complexity that cannot be easily resolved by comparing the existing different data sets.

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Paper number 94GL00177
0094-8534/94/94GL-00177$03.00

The isotopic data set

We combined data from the Groningen and Oxford ^{14}C databases; bone sample statistics were improved by adding data from the Heidelberg lab, also, some Swedish material was added. We analysed 905 bone, 2541 charcoal, and 1174 wood samples. By analysing such a large data set, which samples material quasi-randomly and covers a wide range of plant species (including a second level of sampling through the food-chain to bone collagen), a wide geographical range (most of Europe and some of the Middle East), and a wide time range (the whole of the Holocene), we have been able to detect a relatively large underlying variation which shows a clear regional pattern in Europe and the Middle East, and which appears to correlate well with a complex of climatic parameters. Bone collagen closely reflects the overall isotopic composition of the food intake and thus of the initial plant source, with a systematic shift of approximately $+5‰$ [Schwarcz, 1991]. In the case of wood and charcoal all $\delta^{13}C$'s more positive than $-18‰$ were rejected, and for bone only $\delta^{13}C$'s between -17 and $-23‰$ were used, in order to exclude dietary C_4 plant signals (although not common in Europe), and bones contaminated with humic acids. No corrections were made for the global change in the $\delta^{13}C$ of atmospheric CO_2, or elevational CO_2 pressure differences, nor were the wood samples split into coniferous and deciduous species.

Results and discussion

The validity of our approach requires the following: i) The sampling should not be significantly biassed by being restricted to the choice of archaeological material as received. ii) Where biasses exist, the variation should be small in comparison with the variation over space. For example, we need to show that variation over time [Becker et al., 1991; Toolin and Eastoe, 1993] is small compared to the variation between regions. Figure 1 shows the temporal

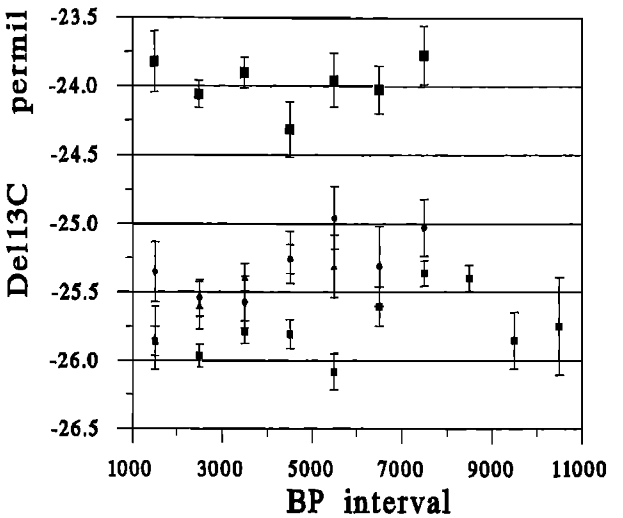

Fig.1. Temporal variation within the Holocene for charcoal samples from the Netherlands (▪), Germany (◆), Ireland (▲), and Spain (■). Note the separation between Spain and the other countries. Means and error bars are plotted per 1000 year interval; only Groningen data was used in this analysis.

variation in charcoal for four countries during the Holocene: the three more northern countries have an overlapping range from −25 to −26‰; Spain centres around −24‰. This in itself is an indication of regional variation which is stronger than the temporal variation. The regional $\delta^{13}C$ variation in bone is illustrated in Figure 2; charcoal shows a shift from −25.8 (Netherlands) to −22.9‰ (Libya), and wood from −27.5 (United Kingdom) to −23.8‰ (Israel / Jordan). In Figure 3 the average $\delta^{13}C$ of charcoal, wood and bone samples per country are plotted against variables such as present-day mean July temperature, relative humidity, hours of sun, and precipitation in May and July (weather stations from Müller [1982] were taken as much as possible representative for the individual countries). In all cases responses are less pronounced in charcoal than in bone and wood. We feel that one of the reasons for the clear response in bone is the chemical and thus isotopical homogeneity of the extracted collagen, which sets it apart from the in that respect more variable charcoal and wood samples [Wilson and Grinsted, 1977; Toolin and Eastoe, 1993]. We find a strong correlation with all parameters except May precipitation (Table 1). For instance, for bone the correlation parameters with sunshine are $p < 0.001$, $r = 0.84$; and the correlation with May precipitation is absent ($p = 0.4675$, r

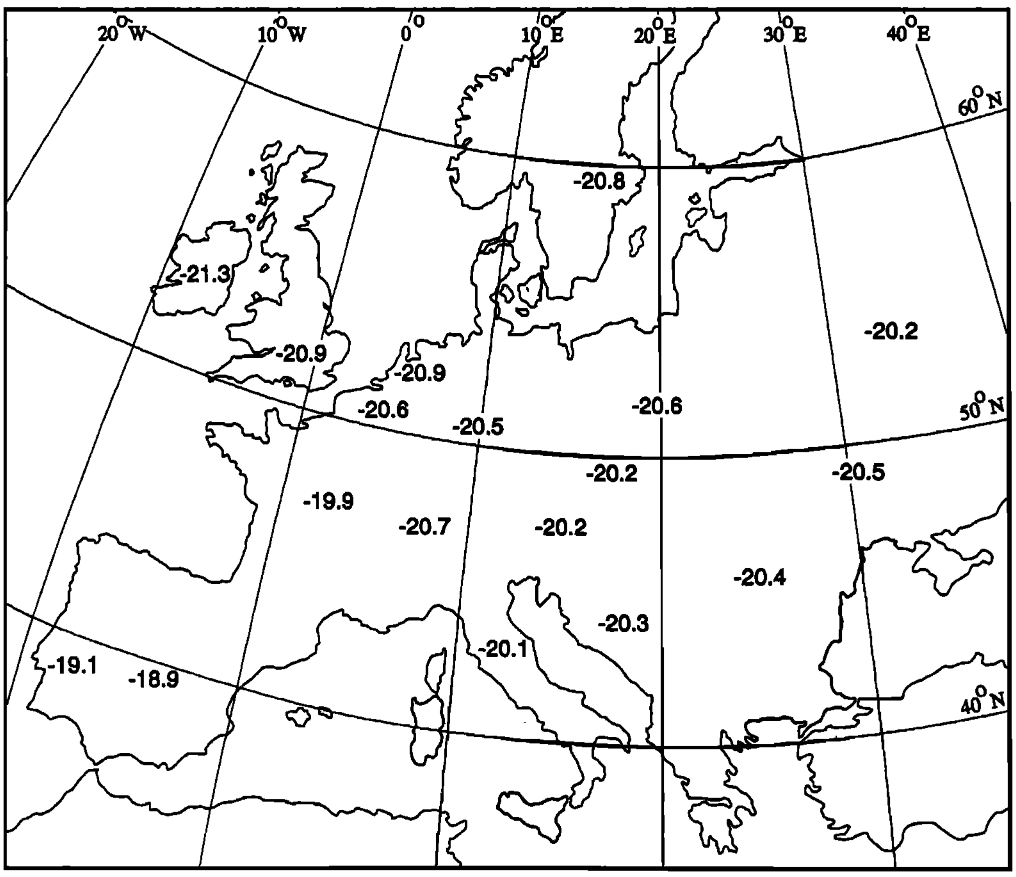

Fig. 2. The pattern of $\delta^{13}C$ variation in Europe as observed in bone. Values are the mean $\delta^{13}C$ per country or region (eg, Northern Ireland is combined with the Republic of Ireland; the countries of the former Yugoslavia are taken as one region); errors are in the order of 0.2‰. The observed trend in Europe can be ascribed to a combination of a latitudinal change in the climatic parameters as discussed in the text, and a similar shift from an Atlantic zone in the west to a more Continental zone in the east. Charcoal and wood show similar patterns.

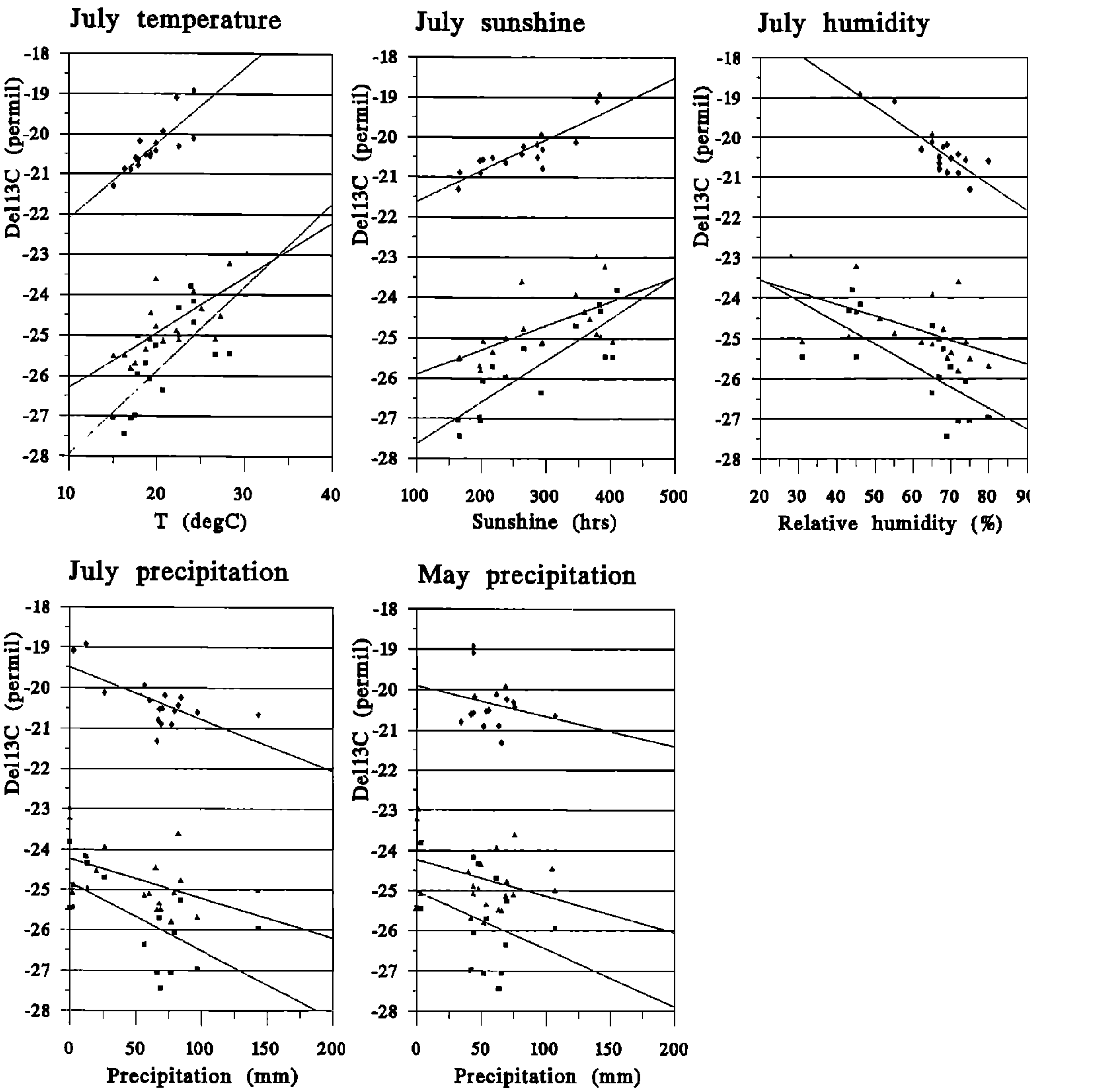

Fig. 3. The relationship between the $\delta^{13}C$ of bone (◆, top regression lines), charcoal (▲, middle) and wood (■, bottom) samples, respectively, and present-day mean July temperature, relative humidity, hours of sunshine, and precipitation in May and July. Average n is about 85.(range 13-850). Observe that slopes of the bone and wood sub-sets are quite similar, and that the charcoal slopes are much less pronounced. Note that the May precipitation lines do not represent significant correlations.

= 0.20). The slope for bone samples is 0.18±0.04‰ per °C, and −0.06±0.01‰ per % relative humidity; in wood we find 0.21±0.06‰ per °C and −0.06±0.01‰ per % relative humidity, respectively. These values are similar to those found in studies of individual tree species from non-marginal American contexts (slopes in the order of +0.2 to 0.3‰ per °C, and about −0.03‰ per % relative humidity; Stuiver and Braziunas [1987]). These effects could be caused by i) a *direct* effect of an environmental parameter on the isotopic fractionation during the photosynthetic process, or ii) by *indirectly* changing the physiological (eg. hormonal) response which then modulates the photosynthetic process. The fact that, in a single tree, the isotopic fractionation varies by 1-2‰ throughout the season [Leavitt and Long, 1991], and thus with the rate of growth, attests to a close relationship of fractionation with metabolic rate. As said in the introduction, current theory regarding photosynthetic fractionation is not unequivocal, preventing closer scrutiny of the effects of the individual parameters on the observed fractionations.

Since the start of radiocarbon dating the results of thousands of isotopic measurements have accumulated in ^{14}C laboratory data bases. The results of our study imply that high-quality information can be extracted from these data sets, which could be useful to resolve past spatial and temporal climatic variations, eg, similar to Becker et al. [1991].However, sampling strategies need to be developed with sufficient care.

Table 1. Summary of the linear regression statistics for the relations between bone, charcoal and wood $\delta^{13}C$ and the climatic parameters.

Bone n = 905, 18 regions	slope	error	p slope	r
July temperature	0.181	0.039	<0.001	0.781
July humidity	−0.061	0.011	<0.001	0.835
July hrs sun	0.008	0.001	<0.001	0.838
July precipitation	−0.013	0.003	<0.001	0.747
May precipitation	−0.006	0.008	0.468	0.195
Charcoal n = 2541, 22 regions	**slope**	**error**	**p slope**	**r**
July temperature	0.127	0.031	<0.001	0.690
July humidity	−0.027	0.010	0.027	0.519
July hrs sun	0.006	0.002	0.007	0.613
July precipitation	−0.009	0.004	0.045	0.462
May precipitation	−0.009	0.006	0.045	0.321
Wood n = 1174, 16 regions	**slope**	**error**	**p slope**	**r**
July temperature	0.214	0.055	0.003	0.738
July humidity	−0.055	0.014	0.002	0.709
July hrs sun	0.011	0.002	<0.001	0.837
July precipitation	−0.018	0.005	0.006	0.647
May precipitation	−0.015	0.010	0.190	0.379

Conclusions

In summary, in a uniquely large isotopic dataset which averages over many individual effects, we have made the following observations: i) A strong correlation exists between a complex of climatic factors and carbon fractionation throughout the whole of Europe and the Middle East. The effect is robust enough to be evident regardless of plant species. ii) The effect can be traced through the terrestrial food chain. iii) The consistent and clear regional variation observed is stable throughout the Holocene, i.e. the regional variation is far exceeding the temporal variation.

Acknowledgements. We would like to thank Bernd Kromer (Heidelberg) and Kerstin Lidén (Stockholm) for providing data.

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(Received: 7 September 1993;
accepted: 21 October 1993).